

THE HEAT OF OXIDATION OF METHYL LINOLEATE AND  
ETHYL LINOLENATE AS DETERMINED WITH AN  
ICE CALORIMETER

by

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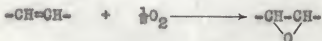
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## INTRODUCTION

The process of oxidation of fats and fatty acids with air or oxygen is of great significance from both an industrial and biological standpoint, and its attempted understanding has been the subject of many years of scientific investigation. Prior to 1941, with a few exceptions, research was conducted on the oils themselves, and most of the work was concerned with the changing properties of the oil as the oxygen was absorbed. Since the oils are glycerides and very complex, it was usually impossible to explain the numerous phenomena that occurred. To complicate the situation further, the analytical methods used were usually unsatisfactory when applied to oxidized oils.

Prior to 1897, molecular oxygen was presumed to break down, to a small extent, to atomic oxygen, and this active oxygen was supposed to be responsible for the slow oxidation of unsaturated compounds (15). According to the Engler and Bach hypothesis (6) the autoxidation by atmospheric oxygen is molecular and not atomic. A molecule of oxygen adds at the double bond to form a peroxidized compound, and this compound could in turn oxidize another oxidizable material.

Fokin (12) proposed a theory in which the first step in the autoxidation of an ethylenic bond was presumed to occur through the formation of an ethylene oxide ring:

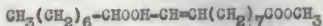
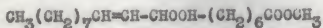


In substantiation of the theory of ethylene oxide formation during autoxidation, Pokin considered it, along with experimental data, from a kinetic standpoint.

Staudinger (18) proposed a theory of autoxidation based on the assumption that the peroxide reaction proposed by Engler and Bach was probably not the first, but the second step in the autoxidation of compounds with ethylenic bonds. Diphenylethylene peroxide isolated by Staudinger was found to be relatively stable, but the product of first addition of oxygen could not be isolated and was unstable. It exploded when heated to 40-50°. He pointed out that the term moloxide should be used for the primary oxidation product and the term peroxide for the four-membered heterocyclic ring.

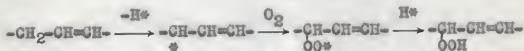
In 1928 Stephens (19) reported the isolation of a peroxide of cyclohexene which he obtained by treating cyclohexene with oxygen in daylight, and he assumed that it was saturated. However, research by Criegee, Pilz, and Flygare (4), and by Farmer and Sundralingam (10), established the fact that Stephens' product was a hydroperoxide and that a double bond was present. To Farmer and his co-workers is due the credit for the hydroperoxide hypothesis of autoxidation. Farmer and Sutton (11) prepared methyl oleate hydroperoxide by oxidizing methyl oleate with oxygen while irradiating it with ultra-violet light. The hydroperoxide was isolated by molecular distillation. The hydrogen and iodine values indicated that the hydroperoxide retained the olefinic unsaturation and that it was formed by the substitution at one or the other  $\text{CH}_2$  groups adjacent to the double bond. Hydrolysis of

the reduction product of the hydroperoxide gave a mixture of 8- and 11-monohydroxystearic esters. From this information two structures were assigned to the methyl hydroperoxide oleate:



Recently, Swift, Dollear, and O'Connor (20), by low temperature crystallization of oxidized methyl oleate from acetone, obtained the same unsaturated hydroperoxide as Farmer but at about 90 per cent purity.

Farmer (7) pointed out that this alpha-methylenic reactivity was typical of the reactions with olefins of free phenyl radicals produced from dibenzoyl peroxide and other materials. It appears to follow a free-radical mechanism sometimes depicted as shown below:



According to Farmer, Koch, and Sutton (9), such detachment of the alpha-methylenic hydrogen atom of the free radical mechanism will enable the resonating radical to assume greater stability:



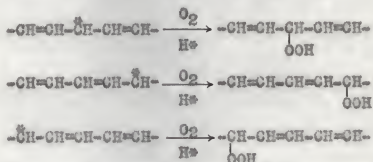
This shift of the double bond has been demonstrated spectrophotometrically (9) in polyunsaturated compounds.

It is difficult to explain the ease with which the hydroperoxides form by such a simple mechanism as given above, since,



sorbed, it is sufficient to initiate the chain reactions.

Bolland and Koch (3) have shown that the monohydroperoxide formed in the oxidation of ethyl linoleate contained about 70 per cent conjugated diene isomers. On the basis of the free radical mechanism and a resonating structure, it would be expected to contain three isomeric forms of the hydroperoxides.



Bergstrom (1), however, failed to isolate the 11-hydroxystearic acid when the oxidation products of methyl linoleate were hydrogenated. He did obtain the 9- and 13- hydroxystearic acids by chromatographic separation. The obvious conclusion that no unconjugated 11-hydroperoxide was formed is doubtful, as there exists definite spectroscopic evidence (14) that systems of the type  $R_1\text{CH=CH-CHOOH-CH=CHR}_2$  can undergo conjugative isomerization during catalytic reduction.

In the present thesis an attempt was made to determine the validity of the chain reaction mechanism set forth by Farmer (7) by a study of the heat of oxidation of the unsaturated fatty acid esters, methyl linoleate, and ethyl linolenate. It was also assumed that, during the initial periods of autoxidation, only the hydroperoxide was formed to any great extent. With these two points in mind, an attempt was made to add to the understanding

of the mechanisms of autoxidation.

## EXPERIMENTAL PROCEDURE

### Reagents

The methyl linoleate and ethyl linolenate used in these experiments were prepared by the debromination of tetrabromostearic acid and hexabromostearic acid respectively according to the method of Rollett (17).

Preparation of Methyl Linoleate. Three hundred g of potassium hydroxide were placed in a five-liter round-bottom flask, 1200 ml of ethyl alcohol and 100 ml of water were added, and the mixture was heated to near boiling on a steam cone. One thousand g of corn oil were added to the hot solution, attaching a condenser and refluxing for 30 minutes. The hydrolysate was cooled to about 40° in a stream of tap water and 1300 ml of cold distilled water added. With continued cooling and agitation, 550 ml of cold concentrated hydrochloric acid were added in small portions. The cold mixture was then transferred to a large separatory funnel and shaken vigorously to insure complete decomposition of the soaps. The fatty acids were washed twice with about one liter of distilled water, care being taken to avoid emulsification. One liter of redistilled petroleum ether was added, and the fatty acids were washed again. After the water had been drawn off, the fatty acids were placed in a five-liter round-bottom flask to which about 50 g of anhydrous sodium sulfate were added. One liter of redistilled petroleum ether was then added and the solution allowed to stand

overnight at  $-5^{\circ}$ . The saturated acids and the sodium sulfate were filtered off, and one liter of redistilled petroleum ether was added to the filtrate which was then ready for bromination.

The five-liter flask containing the solution of fatty acids was clamped firmly into an ice-salt bath, the flask being at least three inches above the bottom of the bath to provide proper cooling. A mechanical stirrer with sufficient speed and power to produce good mixing was adjusted to about one-half inch from the bottom of the flask. Bromine was added from a separatory funnel at such a rate that the temperature of the reaction mixture at no time exceeded  $10^{\circ}$ . About 580 g of bromine were required for complete saturation, as indicated by the persistence of a bromine color. The flask was corked tightly and allowed to stand overnight at  $-5^{\circ}$ . The crystalline crude tetrabromostearic acid was collected on a Buchner funnel, washed with redistilled petroleum ether, and transferred to a dry five-liter round-bottom flask. Five liters of redistilled petroleum ether were added, and the tetrabromostearic acid was brought into solution by refluxing on a steam cone. When solution was complete, it was filtered through a warm Buchner funnel using oversized filter paper. The filtrate was allowed to stand overnight at  $-5^{\circ}$ . The product was filtered on a Buchner funnel and washed with redistilled petroleum ether. The white crystals were dried at room temperature.

Two hundred g of tetrabromostearic acid and 200 g of granular zinc were mixed together and placed in a dry, ground-neck, round-bottom flask. A condenser was attached, and 200 ml of methyl alcohol were added and the acid dissolved by warming care-

fully on a steam cone. Cooling in a stream of tap water was necessary to control the initial reaction, after which the mixture was allowed to reflux for two hours on the steam cone. The reaction mixture was cooled and poured into a separatory funnel containing 500 ml of distilled water. A small amount of hydrochloric acid was added to decompose any zinc soaps which might be present, and the mixture was shaken vigorously and allowed to stand until the ester had separated completely. The aqueous phase was then drawn off and extracted twice with 200 ml of petroleum ether. The ester and ether solution was then washed with 500 ml of two per cent sodium carbonate solution and twice with 100 ml of cold water. The washed ether solution was dried over anhydrous sodium sulfate, filtered, and the solvent removed by means of a water pump. The ester was then distilled under reduced pressure.

Preparation of Ethyl Linolenate. Three hundred g of potassium hydroxide were placed in a five-liter round-bottom flask, 100 ml of distilled water were added, and the mixture was carefully agitated to facilitate solution. When solution was complete, the flask and its contents were cooled to room temperature, 1200 ml of ethyl alcohol were added, followed by 1000 g of raw linseed oil. The mixture was refluxed for 30 minutes. The hydrolysate was cooled to about 40°, diluted with 100 ml of cold distilled water, and acidified with 550 ml of cold concentrated hydrochloric acid. The acid was added in small portions with constant cooling and agitation. The cold mixture was then placed in a large separatory funnel and shaken vigorously to insure complete decomposition of the soaps. Next, the fatty acids were

washed twice with one liter volumes of distilled water. One liter of diethyl ether was added, and the fatty acids were washed again with one liter of distilled water. After the last washing, the fatty acids were drawn off into a five-liter round-bottom flask. Fifty g of anhydrous sodium sulfate were added, and the solution was allowed to stand overnight at  $-5^{\circ}$ . The saturated acids and the sodium sulfate were filtered from the cold solution, and an additional liter of diethyl ether was added to the filtrate. It was then ready for bromination.

The five-liter round-bottom flask containing the still cold filtrate was clamped firmly in an ice-salt bath and a mechanical stirrer was introduced to keep the solution in a constant state of agitation. Bromine was added from a small separatory funnel at such a rate that the temperature of the mixture would not rise above  $10^{\circ}$ . The bromination was complete when the mixture had a persistent bromine color due to a slight excess of bromine. The flask was corked tightly and allowed to stand overnight at  $-5^{\circ}$ . The crude, crystalline hexabromostearic acid was collected on a Buchner funnel, washed with diethyl ether, and recrystallized from hot benzene. The crystals were dried at room temperature.

Two hundred g of hexabromostearic acid and 200 g of granular zinc were mixed together and placed in a dry, ground-neck, round-bottom flask. A condenser was attached, and 200 ml of absolute ethyl alcohol, containing a few drops of concentrated sulfuric acid to catalyze the reaction, were added and the acid dissolved by warming carefully on a steam cone. Cooling in a stream of tap water was necessary to control the initial reaction, after

which the mixture was allowed to reflux for two hours on the steam cone. The reaction mixture was then cooled, and 200 ml of petroleum ether and 500 ml of distilled water were added forming a two phase system. The aqueous phase was then drawn off and extracted twice with 200 ml of petroleum ether. The ester and ether solution was then washed with 500 ml of two per cent sodium carbonate solution and twice with 100 ml of cold water. The washed ether solution was dried over anhydrous sodium sulfate, filtered, and the solvent removed by means of a water pump. The ester was then distilled under reduced pressure.

### Apparatus

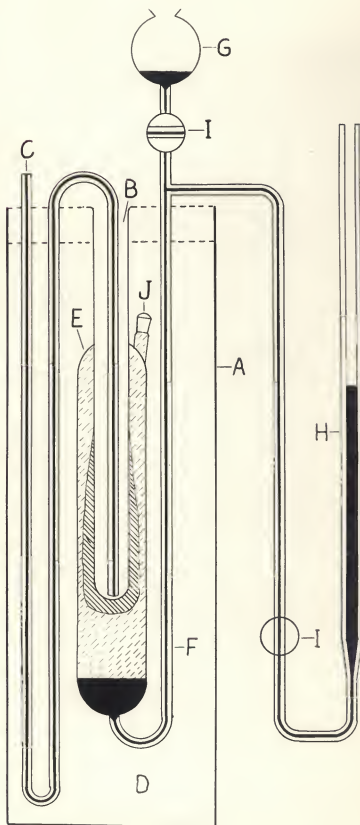
Construction of the Ice Calorimeter. A diagram of the ice calorimeter is shown in Plate I. All parts except the ice bath chamber, A, were made of Pyrex glass. The central well, B, was provided to receive samples of the unsaturated fatty acid esters to be oxidized. Oxygen or nitrogen, as the case may be, was bubbled into the sample through capillary C. The calorimeter was insulated by an ice bath, D, kept at 0°. The burette, H, was connected to the system through the lower stopcock, I. This burette had a capacity of one ml and was calibrated in 0.01 ml divisions. While in use, the ice bath chamber was well insulated with rock wool.

Filling the Calorimeter with Mercury and Water. After the system was thoroughly cleaned, E was filled about one-sixth full with mercury by pouring it through the reservoir, G. Water that had been boiled and cooled under vacuum to remove the dissolved

# EXPLANATION OF PLATE I

- A. Metal ice bath chamber
- B. Central well for sample
- C. Gas inlet tube
- D. Ice bath
- E. Outer jacket of calorimeter
- F. Capillary tubing for mercury
- G. Mercury reservoir
- H. One ml burette
- I. Glass stopcocks
- J. Ground-glass joint and stopper

## PLATE I



gases was admitted through the ground-glass joint, J, until E was completely filled. The ground-glass stopper was replaced into J, care being taken that no air space was left in E, and sealed with collodian. The rest of the system (F and H) was then filled with mercury.

Formation of the Ice Mantle. By admitting solid carbon dioxide in the central well, an ice mantle was formed around the outside of B, inside the outer jacket of the calorimeter, E. This formation of ice forced the mercury out of the internal system and showed a rise in H. The amount of ice formed was regulated by measuring the change of the volume of mercury in the burette. About two and one-half ml change was sufficient ice for each experiment. The ice mantle was usually frozen in about one and one-half hours.

### Methods

Oxidation of a Sample. After freezing an ice mantle in the calorimeter and allowing to stand overnight, a sample of methyl linoleate or ethyl linolenate, from two to seven g, was accurately weighed and placed into the central well, B. From 0.012 to 0.016 g of a cobalt naphthenate drier was added to catalyze the reaction. The gas inlet tube was replaced, and nitrogen passed into the sample at about 100 bubbles per minute. The addition of nitrogen was prolonged until the sample had reached 0° which usually took about 30 minutes. The stabilization of the mercury column in the burette indicated when this point was reached. The flow of nitrogen was then cut off, and a flow of oxygen was intro-

duced. The latter also was passed in at the rate of about 100 bubbles per minute. Readings of the burette were taken about every ten minutes until the reaction had begun, then every few hours until the reaction was stopped. During this time, the ice bath, surrounding the calorimeter, was repacked every six hours with clear ice and distilled water. This procedure was necessary to minimize the heat exchange.

Determination of Oxygen Absorbed. After the sample had been oxidized in the calorimeter, about 0.1 g was removed and accurately weighed into a 125 ml glass stoppered flask and dissolved in 3 ml of a 1:1 mixture of chloroform and glacial acetic acid. After solution was complete, one ml of a saturated solution of potassium iodide was added and the flask shaken for one minute. The stopper and side of the flask were washed down with 5 ml of distilled water. The excess iodine was titrated with 0.01 N sodium thiosulfate solution until the solution was yellow. Three drops of starch indicator were added and the titration continued until the solution was clear, indicating the end point. The necessary calculations for the determination of the oxygen absorbed were as follows:

$$\frac{(\text{ml of titration})(N \text{ of thio})(\text{mole wt of sample})}{(\text{sample weight in g})(1000)(2)} = \text{mole of } O_2 \text{ absorbed/mole of ester.}$$

Calculations of the Heat of Oxidation. The change in volume of the mercury in the burette was calculated to one mole of the ester by the following formula:

$$\frac{(V \text{ in ml as read})(\text{mole wt of sample})}{\text{sample weight in g}} = V_1$$

where

$V_1$  = ml of mercury change per mole of ester.

The ml of mercury change per mole of ester were plotted against the time in hours, and the best straight line was drawn through these points. The volume determined from this straight line at the time the sample was analyzed for the oxygen absorbed was used to calculate the heat of oxidation. The amount of heat required to melt the ice in the calorimeter for a mole of ester was determined by the following formula:

$$\frac{(878.06)(V_1)}{1000} = \text{kcal/mole of ester}$$

The value, 878.06, was calculated from the density of ice at 0° as reported by Ginnings and Corruccini (13) as 0.91671 g per ml and the density of water at 0° as reported by Dorsey (5) as 0.999868 g per ml, as follows: One g of ice melts to one g of water at 0° with the absorption of 79.6661 calories (16). Therefore

$$\begin{aligned}\Delta V &= \frac{1}{0.91671} - \frac{1}{0.999868} \\ &= 0.09073 \text{ ml}\end{aligned}$$

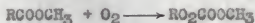
where

$\Delta V$  = change in specific volume,

then

$$\frac{79.6661}{0.09073} = 878.06 \text{ cal per ml.}$$

By dividing the kcal per mole of ester by the mole of oxygen absorbed per mole of ester, the heat of oxidation, given as kcal per mole of oxygen absorbed, of the following reaction was determined.



The heat content,  $\Delta H$ , was negative due to the heat evolved in the reaction.

### RESULTS

The oxygen used to oxidize the sample of ester was first dried by bubbling it through concentrated sulfuric acid at the rate of approximately 100 bubbles per minute before it entered the reaction chamber of the calorimeter.

Four samples of methyl linoleate were oxidized, three of which appear in Table 1. After the oxygen absorbed in sample I had been determined, it was further oxidized for an additional 24 hours. At the end of this period, the heat of oxidation was calculated to be -116.0 kcal.

Table 1. The heat of oxidation of methyl linoleate and ethyl linolenate.

Sample number	Sample weight	V in ml/ sample weight	$V_1$	$\text{O}_2$ absorbed per mole of ester	$\Delta H$ in kcal
Methyl linoleate					
I	6.8699	0.240	10.30	0.14	-64.6
II	3.4226	0.157	13.60	0.17	-69.7
III	3.7168	0.209	17.10	0.22	-68.2
Ethyl linolenate					
IV	2.3400	0.110	14.50	0.19	-67.0
V	2.3177	0.084	11.40	0.15	-66.6
VI	2.2753	0.107	13.07	0.17	-67.5

Samples I, II, and III were oxidized for periods of 23.7, 23.3, and 22.3 hours, respectively. At the beginning of the oxidation periods samples II and III contained no detectable peroxide, but sample I had been partially oxidized to 0.02 mole of oxygen per mole of ester before it was placed in the calorimeter. At the end of the oxidation period of this sample, the peroxide present was found to be 0.16 mole of oxygen per mole of ester. This gave a total of 0.14 mole of oxygen absorbed during the reaction period.

The plot of ml of mercury per mole of ester against time in hours, to determine the best value for  $V_1$  at the end of the oxidation period, is given in Fig. 1 for methyl linoleate and in Fig. 2 for ethyl linolenate. The top line of the two very close curves in Fig. 2 is for sample V.

Four samples of ethyl linolenate were oxidized, and three of these appear in Table 1 also. The one sample that does not appear in the table was oxidized to a peroxide value of only 0.09 mole of oxygen per mole of ester giving a heat of oxidation value of -83.0 kcal.

Samples IV, V, and VI were oxidized in the calorimeter for periods of 11.9, 10.7, and 12.4 hours, respectively. These samples contained no detectable oxygen as peroxides at the beginning of the oxidation periods in the calorimeter.

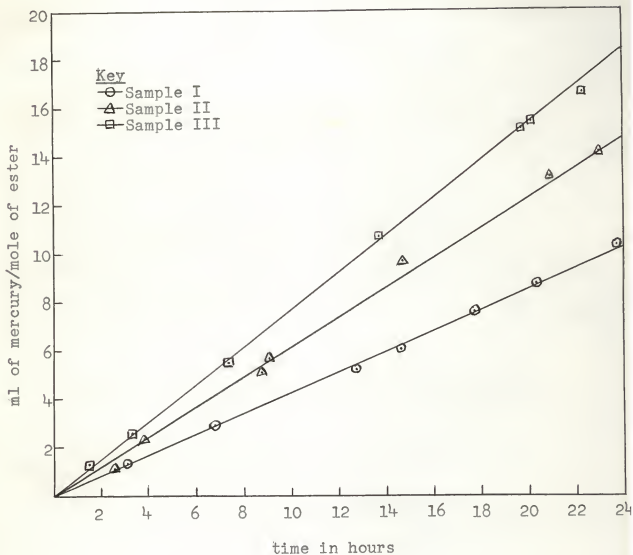


Fig. 1. The change in volume of mercury during reaction periods.

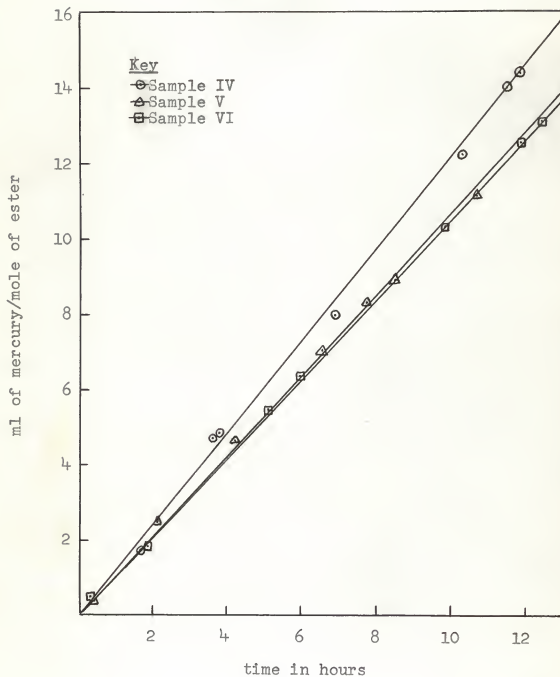


Fig. 2. The change in volume of mercury during reaction periods.

## DISCUSSION

The heat of oxidation value reported in this paper, -67 kcal at  $0^{\circ}$ , seemed to be in close agreement with the value, -53 kcal of Bolland and Gee (2) determined by oxidation of ethyl linoleate and linolenate at  $40^{\circ}$ . The difference is probably due to the different temperatures at which each value was determined.

After sample I had been analyzed for the oxygen absorbed, it was further oxidized for an additional 24 hours. The oxygen determination showed a value of 0.07 mole of oxygen absorbed as peroxide and a heat of oxidation of -116.0 kcal. This low peroxide value and high heat of oxidation indicated secondary oxidation products were forming and may also have included some heat of polymerization.

The sample of ethyl linolenate that was oxidized to a peroxide value of 0.09 mole of oxygen had a heat of oxidation value of -83.0 kcal. This would tend to indicate that the initial reactions in autoxidation are of a chain mechanism in character that was postulated by Farmer (8). In other words, a high amount of energy would be necessary to initiate the reaction, but the overall reaction of peroxidation would require fairly small amounts of energy. This also showed that the peroxide formation in the unsaturated esters, using a cobalt naphthenate drier at  $0^{\circ}$ , would be comparable to the peroxide formation of the esters without the drier, at higher temperatures.

The enzyme, lipoxidase, prepared by the extraction, with water, of defatted soybean meal, was found to be unsatisfactory

as a catalyst in the oxidation process. It appeared that the enzyme itself required a large amount of energy, thereby giving inaccurate results.

An error of 0.01 mole of oxygen per mole of ester in the peroxide determination used in this work would cause an error of about 5 kcal in the range of the heats of oxidation reported. Another error could exist due to the heat leakage of the calorimeter. The latter was determined by passing oxygen through a sample of methyl linoleate that had been oxidized without a catalyst at 30° to a peroxide value of approximately 0.3 mole of oxygen per mole of ester. Therefore, if there was any reaction, it would be too small to measure over a 24-hour period. This heat leakage was calculated to be 0.2 kcal in 24 hours. This value was not subtracted from the original value because it is negligible in comparison to the large experimental error in the peroxide determination.

An error due to supercooling was eliminated by freezing the ice mantle and allowing it to come to equilibrium. This error was considerable during preliminary runs of the calorimeter and gave results of opposite signs of what they should have been, indicating the formation of more ice.

By passing the oxygen through concentrated sulfuric acid to dry the gas, it was possible to keep water from entering the reaction chamber. Therefore, no heat of mixing needed to be calculated.

## SUMMARY

The heat of oxidation of methyl linoleate and ethyl linolenate was found to be -67 kcal with a possible error of  $\pm 5$  kcal, as calculated from the physical data obtained by the oxidation of these two unsaturated esters in the ice calorimeter described in this paper.

It was found that the method used to determine the peroxide value was inaccurate and could cause a large error in the calculations of the heats of oxidation.

A large amount of energy was necessary to initiate the oxidation reaction, but the overall peroxidation required relatively little energy. This supports the chain reaction mechanism theory of Farmer.

## ACKNOWLEDGMENT

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## Date Due

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